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Derivatives of
3,3-Dimethyl 2-Cyan 2-Carboxethyl
Cyclopentanone

Chemistry

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DERIVATIVES OF
3,3-DIMETHYL 2-CYAN 2-CARBOXETHYL CYCLOPENTANONE

BY

CHARLES KAY HEWES
B. S. University of Illinois
1912

THESIS

Submitted in Partial Fulfillment
of the Requirements for the
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IN CHEMISTRY

IN

THE GRADUATE SCHOOL
OF THE
UNIVERSITY OF ILLINOIS

1914

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UNIVERSITY OF ILLINOIS

THE GRADUATE SCHOOL

May 25 1914.

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Charles Kay Hewes

ENTITLED DERIVATIVES OF 3,3-DIMETHYL 2-CYAN 2-CARBOXETHYL CYCLOPENTANONE

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Master of Science

William A Noyes
In Charge of Major Work

Wm A. Noyes
Head of Department

Recommendation concurred in:

Committee
on
Final Examination

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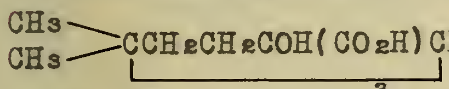
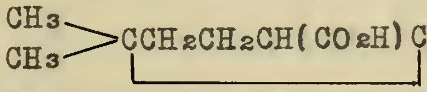
Part I.

HISTORICAL AND THEORETICAL

2,3,3 - Trimethylcyclopentanone[1] has been identified with a ketone previously obtained from camphoric acid by a series of easily interpreted reactions. This ketone, so important in its relation to camphor and camphoric acid, was prepared by the following method. The tricarboxylic ester resulting from the union of one mol of the ethyl ester of γ - bromoisocaproic acid and one mol of the sodium salt of the ethyl ester of methyl malonic acid, was saponified, then heated to drive out carbon dioxide, and finally distilled with lime.

This same ketone[2] was previously prepared by distilling α - hydroxydihydrocampholytic acid,  $\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!C\underbrace{CH_2CH_2COH(CO_2H)CH}CH_3$, with lead dioxide and sulfuric acid. E. B. Harris[3] has also prepared 2,3,3 - trimethylcyclopentanone, in two ways. The first method consists in converting dihydroisocampholytic acid,  $\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!C\underbrace{CH_2CH_2CH(CO_2H)CH}(CH_3)$, into the amide, then into the amine, into the corresponding alcohol, and finally oxidizing this alcohol with Beckman's mixture of sulfuric acid and potassium dichromate, which yielded the ketone. In the second method the ketone was prepared thru pentane tetracarboxylic ester from trimethylene bromide

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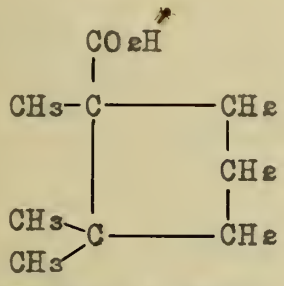
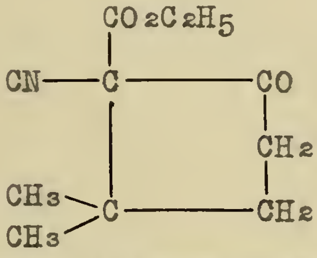
[1] W. A. Noyes, Am. Chem. J. (1900) 23, 128.
[2] Noyes and Shepherd, Am. Chem. J. (1899) 22, 264.
[3] Am. Chem. J. (1896) 18, 692.

and malonic ester, introducing two methyl groups by the method of Perkin and Prentice[1], saponifying, heating the tetracarboxylic acid to 200°, and distilling the resulting dimethylpimelic acid with lime.

Having obtained 2,3,3 - trimethylcyclopentanone[2] from camphor, it was then hoped to effect a synthesis of camphoric acid from the ketone, 3,3 - dimethyl 2 -cyano-2-carboxethylcyclopentanone[3]. Upon sight there is quite a little resemblance between the two structures:



Camphoric acid.



Dimethylcyanocarboxethylcyclopentanone.

W. A. Noyes[4] developed the synthesis of dimethylcyanocarboxethylcyclopentanone by converting isoamyl alcohol successively into the bromide, cyanide, acid, the corresponding lactone, the γ -bromo ester, and the condensation of this ester with the sodium salt of cyanoacetic ester. The reactions are as follows:

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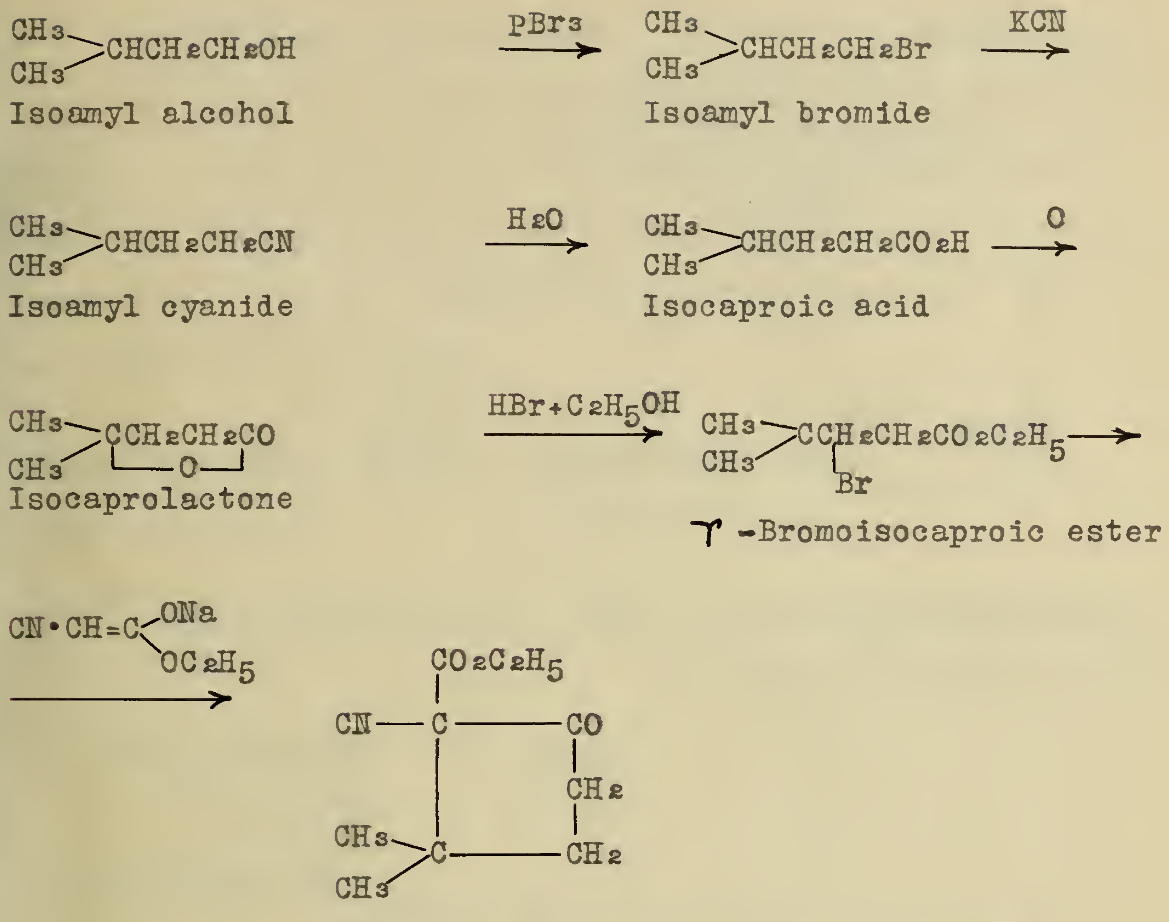
[1] Ber. d. chem. Ges. (1891) 24, 818, 852.
[2] Noyes, Am. Chem. J. (1900) 23, 128.
[3] Noyes, Ibid (1900) 23, 135.
[4] Am. Chem. J. (1899) 22, 259. Also Ibid (1900) 23, 392.



Dimethylcyanocarboxethylcyclopentanone

In this procedure it is necessary to use large quantities of materials, making the operations long and the separations tedious, so that after the method had been tried in the present research, it was abandoned for a simpler and easier one. At first it was thought that isocaprolactone could be prepared by heating terebinic acid with dilute sulfuric acid, as shown by Erdman[1], but the yields were not good. Then Blaise's[2] method suggested itself for the preparation of isocaprolactone from acetone and bromosuccinic acid but

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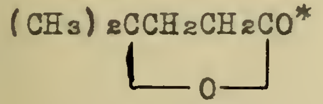
[1] Ann. (1885) 228, 81.
[2] Comptes rend. (1898) 126, 349.

here the yield was likewise poor. Finally the method proposed by Gordon[1], the action of methyl-magnesium iodide on levulinic ester, was tried and found to give fairly good results. In the condensation there was no separation of the hydroxy acid but the lactone was obtained directly. The reactions are as follows:

$$\underset{\text{Levulinic acid}}{CH_3COCH_2CH_2CO_2H} \xrightarrow{C_2H_5OH} \underset{\text{Levulinic ester}}{CH_3COCH_2CH_2CO_2C_2H_5} \xrightarrow{CH_3MgI}$$

$$(CH_3)_2C(OMgI)CH_2CH_2CO_2C_2H_5 \xrightarrow{H_2O} \underset{\gamma\text{-Hydroxyisocaproic ester}}{(CH_3)_2C(OH)CH_2CH_2CO_2C_2H_5}$$



$(CH_3)_2CCH_2CH_2CO^*$ (ring closed through O)

Isocaprolactone

Having prepared 3,3-dimethyl 2-cyano-2-carboxethyl-cyclopentanone by the two methods indicated, i.e., the isoamyl alcohol and levulinic acid methods, it was next hoped to effect its synthesis thru an internal condensation of a derivative of adipic ester[2]. For this purpose isobutylene bromide (one mol) was condensed with the sodium salt of cyanoacetic ester (two mols). The reactions for the condensation are as follows:

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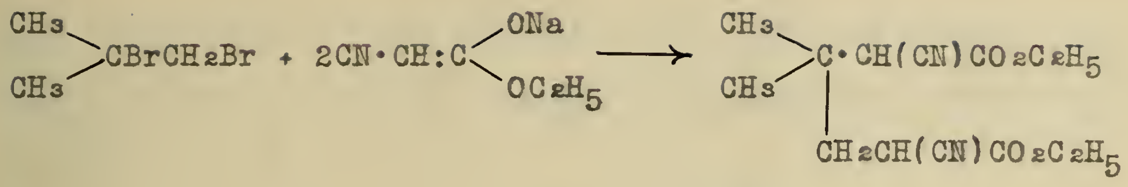
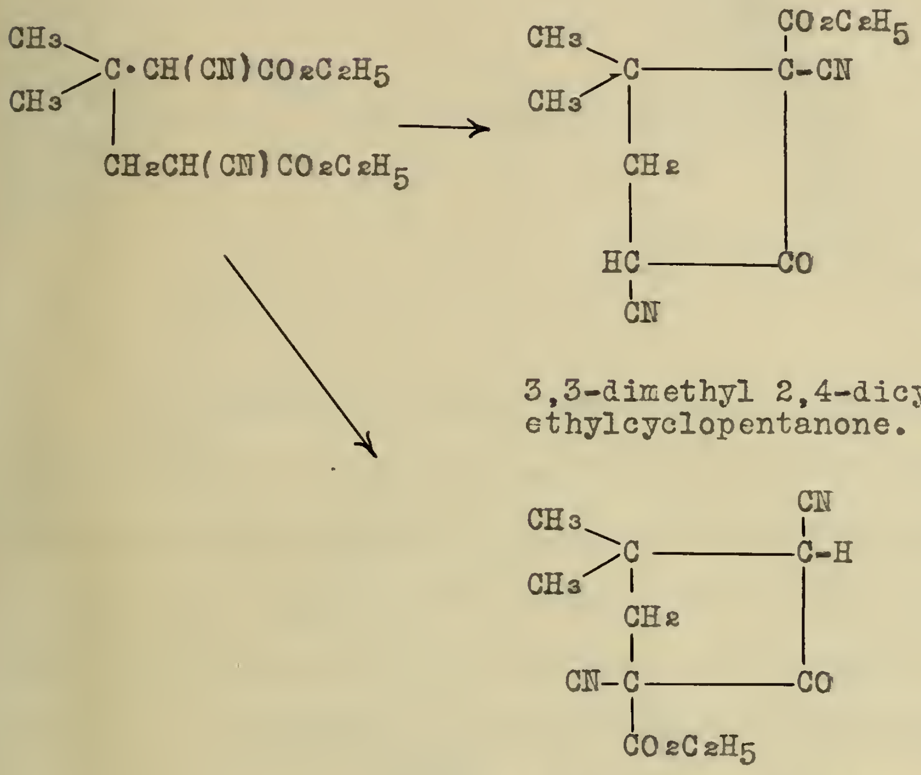
[1] Thesis, University of Illinois (1911).

[2] Bouveault, Bull. Soc. Chem. (1899) iii , 21, 1019, has effected the condensation of ethyl adipate by the action of sodium.

*From this compound to the ketone, the reactions are the same as have been given above.





3,3-dimethyl 2,4-dicyan 2-carboxethylcyclopentanone.

3,3-dimethyl 2,4-dicyano 4-carboxethylcyclopentanone.

In this condensation there resulted a tarry mass[1] that could not be purified.

The structure of 3,3-dimethyl 2-cyano 2-carboxethylcyclopentanone[2] follows from the fact that the methyl ester of γ-bromoisocaproic ester in the condensation with the sodium salt of cyanacetic ester gives the same results as does

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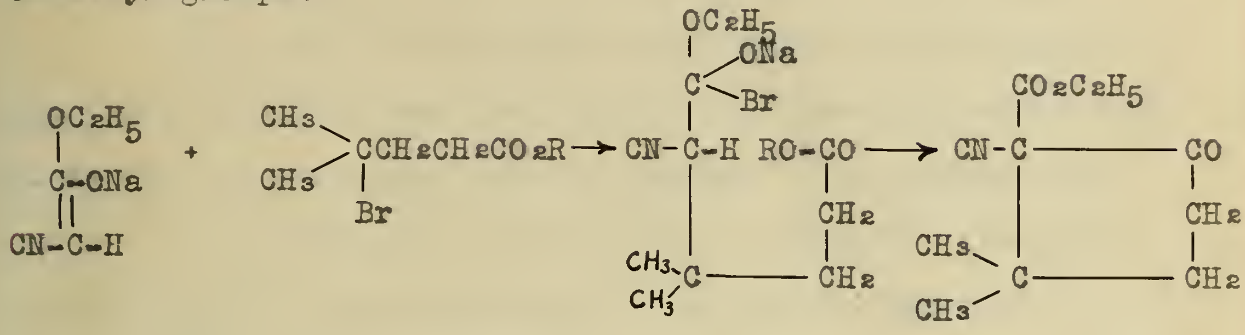
1. Zelinsky, Ber. d. chem. Ges. (1891) 24, 3998, prepared the symmetrical 2,5-dimethyl 2,5-dicyanadipic ester but in this case it is evident that there are no replaceable hydrogen atoms on the α-carbon atoms.
2. Noyes, Am. Chem. J. (1899) 22, 259.

the ethyl ester in the condensation. This is evident from the following reactions, letting "R" designate either methyl or ethyl groups:



Zeissel's[1] method was employed for a quantitative determination of the carboxethyl group in the above ketone. Dimethylcyanocarboxethylcyclopentanone was treated with hydriodic acid (sp. gr 1.7) at 80°. The ethyl iodide resulting from the action was distilled over thru Geissler bulbs containing red phosphorus, into an alcoholic solution of silver nitrate. The precipitated silver iodide corresponded to 87.4 per cent of that demanded by theory.

Dimethylcyanocarboxethylcyclopentanone[2] crystallizes from alcohol in white needles melting at 148°-149°. It is insoluble in water. When heated with hydrochloric acid in sealed tubes at 150° for three hours, the decomposition[3] gives carbon dioxide, acetic acid, and isocaprolactone. Saponification with alcoholic potash yields malonic acid and isocaprolactone. This manner of decomposition, analogous to the

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1. Meyer, Analyse und Konstitutionsermittelung organischer Verbindungen. Page 488.
2. Noyes, Am. Chem. J. (1899) 22, 259.
3. Noyes, J. Am. Chem. Soc. (1901) 23, 396.

"acid decomposition" of acetoacetic ester, is peculiar in that a carbon atom is removed from the ring and replaced by oxygen. Similar cases, however, will be found later in this paper.

The action of Grignard's methyl-magnesium-iodide upon 3,3-dimethyl 2-cyano 2-carboxethylcyclopentanone was studied, following the method used by Gordon.[1] He syphoned an absolute ether solution of methyl-magnesium-iodide (one mol) into an absolute ether solution of the ketone (one mol). It might be stated here that the quantity of ether he used to effect the solution of the ketone (25 cc. for 2.15 grams of ketone) was found to be insufficient. After acidifying and extracting with ether and distilling off the ether, he obtained a small quantity of substance melting at 193.4°. To this compound he assigned the name 1,3,3-trimethyl 2-cyan 2-carboxethylcyclopentanol-1. His directions were followed in every detail mentioned, but several attempts failed to duplicate his work. Then the conditions were varied slightly, using larger quantities of absolute ether and also absolute benzene for dissolving the ketone. The result of five trials, however, failed to give anything but the original ketone.

For the reduction of the ketone to the corresponding cyclopentane derivative, the method of Clemmensen[2] was used. This reduction takes place in the presence of a dilute hydrochloric acid mixture of a ketone and amalgamated zinc. While giving excellent results in many cases, still for this ketone

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1. Thesis, University of Illinois (1911).
2. Orig. Com. 8th Int. Congr. App. Chem. 7, 68, (1912).

the reaction was not noticeable even after boiling the mixture for two days. At the end of this time only the unchanged ketone was recovered.

The oxime of dimethylcyanocarboxethylcyclopentanone was obtained by boiling on the water bath for eight hours, an alcoholic solution of one mol of the ketone, one and one-half mols hydroxylamine hydrochloride, and one and one-quarter mols of sodium hydroxide. A white crystalline substance was recrystallized twice from water. The product melted slightly at 104° and the temperature then rose to 118° where the remainder of the compound melted. This suggested a mixture of the syn and anti forms of the oxime, Harries[1] having observed a similar mixture in an analogous case. There was also the possibility that the product was an isoxazo compound formed by the elimination of one molecule of alcohol from the oxime. A nitrogen determination, however, gave results that checked with the value demanded by theory by the oxime.

Upon saponification of one mol of the oxime with three mols of sodium hydroxide, there was obtained an impure product melting at 127°-129°. At first it was thought that this was malonic acid, the saponification having proceeded as in the case of dimethylcyanocarboxethylcyclopentanone which, with the alcoholic potash, yielded malonic acid and isocaprolactone. The product, however, when heated, failed to give an odor of acetic

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[1] Am. Chem. J. (1896) 18, 694.

acid, which would be formed if malonic acid was present. The calcium salt* of the saponification product, when analyzed, showed that the dibasic acid had been formed by the action of sodium hydroxide upon the oxime of dimethylcyanocarboxethylcyclopentanone.

It has been stated previously that in the synthesis of dimethylcyanocarboxethylcyclopentanone that γ-bromoisocaproic and cyanoacetic esters were used. Esters other than cyanoacetic, however, such as malonic and methyl malonic, have been condensed with γ-bromoisocaproic ester.[1] When an excess of sodium was used with malonic ester, there was obtained 3,3-dimethyl 2,2-dicarboxethylcyclopentanone, while when less sodium was used, the tricarboxylic ester resulted. With methyl malonic and γ-bromoisocaproic esters there was synthesized a triethyl ester of 2,3,3-trimethylhexanoic 1,2,6 acid. It was found that when dimethyldicarboxethylcyclopentanone was saponified with an excess of alcoholic potash, it broke down in the same manner as dimethylcyanocarboxethylcyclopentanone, yielding malonic and hydroxy isocaproic acids.

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*For the preparation and analysis of this salt and for the nitrogen determination made on the oxime I wish to express my thanks to the faculty of Throop College at Pasadena, California, where this work was done.

[1] Noyes, J. Am. Chem. Soc. (1901) 23, 397.

Part II.

EXPERIMENTAL.

A. Preparation of Dimethylcyanocarboxethylcyclopentanone starting with Isoamyl Alcohol.

Hydrobromination of Isoamyl Alcohol.

Into 100 grams (one mol) of isoamyl alcohol was passed 99 grams (one mol) of hydrobromic acid, the latter being generated by passing hydrogen gas thru bromine at 33° and then causing the mixed gases to pass thru a tube containing platinized asbestos heated to 200°-300°. This method of generating hydrobromic acid gives excellent results and was found to be far superior to the method in which bromine is dropped upon a mixture of phosphorus, sand, and water. The isoamyl bromide was allowed to stand over night and was then heated on the steam bath for two hours, 3 cc. of water having been added to prevent the fuming of the hydrobromic acid gas. After cooling it was shaken twice with 1:1 sulfuric acid to remove hydrobromic acid, twice with concentrated sulfuric acid to remove isoamyl alcohol, and finally with a solution of sodium carbonate. After drying over anhydrous sodium sulfate, 48 grams of isoamyl bromide were obtained. As the results were not so good as were desired, the bromide was further prepared by the action of phosphorus tribromide on isoamyl alcohol.

Phosphorus Tribromide.[1]

Into a solution made by dissolving 55 grams of yellow phosphorus in 100 grams of carbon disulfide, was dropped 138 cc. of bromine. After all of the bromine had been added, the solution was distilled from a Ladenburg bulb until a temperature of 165° was reached. The distillate was redistilled up to the same temperature and the total residue, which was sufficiently pure for use, weighed 439 grams, or a yield of 97 per cent of the theory.

Isoamyl Bromide.[2]

To 480 grams of fusel oil (boiling point 128°-132°) was added slowly 439 grams of phosphorus tribromide, with constant cooling. After standing over night, the mixture was warmed on the water bath for two hours, a little water having been added from time to time to prevent the loss of hydrobromic acid. The mixture separated in two layers; the lower layer was separated, distilled up to 140°, and the distillate mixed with the upper layer. It was shaken twice with 1:1 sulfuric acid, twice with concentrated sulfuric acid, once with water, once with a solution of sodium carbonate, and finally with anhydrous sodium sulfate. After filtering, the isoamyl bromide was sufficiently pure for use. The yield was 655 grams, or 91 per cent of the theory.

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[1] Noyes, J. Am. Chem. Soc. (1901) 23, 392.
[2] Noyes, J. Am. Chem. Soc. (1901) 23, 392.

Isocaproic Acid.[1]

308 grams of potassium cyanide were dissolved in 330 cc. of hot water, 1375 cc. of alcohol and 699 grams of isoamylbromide were added. After boiling the solution for twenty-three hours in a five liter flask fitted with a reflux condenser, the solution was poured from the potassium bromide into a second flask containing 385 grams of potassium hydroxide and the boiling was continued for twenty-five hours longer. Then the solution was transferred to an evaporating dish and the alcohol distilled off after several additions of water. The yellowish solid remaining was dissolved in one liter of water and poured into a flask containing 440 cc. of 1:1 sulfuric acid. The isocaproic acid which separated was distilled. The acid solution was extracted several times with ligroin. The isocaproic acid distilled at 190°-193° and the yield was about 82 per cent of the theory.

Isocaprolactone.[2]

In 1025 cc. of water were dissolved 344 grams of isocaproic acid and 171 grams of sodium hydroxide. After cooling, 5.13 liters of a warm 10 per cent solution of potassium permanganate were added in 500 cc. portions at intervals of about an hour. An attempt was made to keep the temperature at 50°-60°, the final decolorization of the permanganate, however, was at 100°. The solution was filtered, the filtrate and washings then concentrated to about 650 cc., and finally poured into

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1. Noyes, J. Am. Chem. Soc. (1901) 23, 392.
2. Ibid.

400 cc. of 1:1 sulfuric acid. After separating the isocaproic acid and isocaprolactone, as a mixture, from the acid solution, the latter was steam distilled until about a liter had passed over. The isocaproic acid and lactone were shaken with this distillate in portions of 300 cc. at a time and then with water in the same manner until five liters had been used. The residual isocaproic acid was distilled and 115 grams of the pure acid were obtained, which was subsequently used for a new oxidation.

The aqueous solution of the lactone was made strongly alkaline with sodium hydroxide and then evaporated on the water bath to a volume of 200 cc. This solution was poured into dilute sulfuric acid, the isocaproic acid and lactone separated, and the solution was extracted three times with ether. The mixture of acid and lactone was exactly neutralized with a 30 per cent solution of potassium hydroxide, 22 grams of dry potassium carbonate added, and the solution was extracted fifteen times with 150 cc. portions of ether. The isocaproic acid remaining in the alkaline solution was recovered. The ether solution of lactone was dried over sodium sulfate and distilled. 44 grams of the lactone (boiling at 200°-204° uncorr.) were obtained, or 34 per cent of the isocaproic acid oxidized.

γ -Bromoisocaproic Ester.[1]

To 65 grams of isocaprolactone were added 200 cc. of absolute alcohol. Into this solution was passed 200 grams of hydrobromic acid gas, generated by the method previously

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[1] Pinner, Ber. d. Chem. Ges. (1886) 19, 514.

described. After standing several hours it was poured into ice water and the ester that separated was washed twice with a little sodium bromide water, dried over sodium sulfate, and filtered. The aqueous portion was extracted several times with petroleum ether. The yield was 98 grams, or 77 per cent of the theory.

Dimethylcyanocarboxethylcyclopentanone.[1]

5.91 grams of sodium were dissolved in 75 cc. of absolute alcohol and the solution cooled. 33 grams of cyanoacetic ester and 57.3 grams of γ-bromoisocaproic ester were then added and the mixture was refluxed for two hours. After cooling it was poured into water and very slightly acidified with sulfuric acid. The solid portion was separated from the aqueous solution and the latter was extracted several times with ether. After distilling under diminished pressure, there remained a brownish residue on cooling. This was crystallized from alcohol. The yield was 5.3 grams, melting at 150° (uncorr.).

B. Preparation of Dimethylcyanocarboxethylcyclopentanone starting with Levulinic Acid.

Levulinic Ester.[2]

A mixture of 200 grams of levulinic acid (impure) and 1750 grams of absolute alcohol was nearly saturated with

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1. Noyes, Amer. Chem. J. (1899) 22, 259.
2. Blaise, Bull. Soc. Chim. (1899) 21, 649.

potassium acid carbonate, it was extracted with ether, the ether after distillation from the levulinic ester was used for another extraction. In all, five such extractions were made in this manner. The yield was 134 grams (boiling at 96°-98° at 17 m.m.), or 54 per cent of the theory.

In the later work a modification of the method of Fischer and Speier[1] was used. 14 grams of dry hydrochloric acid gas were passed into a solution of 200 grams of levulinic acid and 600 grams of absolute alcohol. This mixture was refluxed for four or five hours, the alcohol was distilled off rapidly, and the levulinic ester was distilled under diminished pressure. The yield was 209.5 grams, boiling at 98°-104° under a pressure of 20-25 mm. This yield is 84.5 per cent of that demanded by theory.

Isocaprolactone.

12.5 grams of pure methyliodide, mixed with 200 cc. of absolute ether, was slowly run into a flask containing 4.86 grams of magnesium ribbon which was just covered with absolute ether. It is essential that the magnesium be freshly sandpapered and dried. The last traces of magnesium went into solution on heating gently. The methyl-magnesium-iodide solution so prepared was slowly syphoned over into a flask containing 28.82 grams of levulinic ester and 250 cc. of absolute ether. After warming the mixture for an hour it was poured into a beaker containing 20 cc. of 1:1 sulfuric acid and small pieces

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[1] Ber. d. chem. Ges. (1895) 28, 3252.

of ice. After separating the etherial solution and extracting the aqueous solution, the extract was shaken three times with 20 cc. of a five per cent sulfuric acid solution, and then dried over anhydrous sodium sulfate. The isocaprolactone remaining after the evaporation of the ether was then converted into γ-bromoisocaproic ester by the method previously described.

γ-Bromoisocaproic Ester.

It was thought that it might be possible to convert levulinic ester into γ-bromoisocaproic ester directly, without isolating the intermediate isocaprolactone. 30 grams of methyl iodide in an equal volume of absolute ether were slowly dropped into a flask containing 4.86 grams of magnesium ribbon and 20 cc. of absolute ether. The methyl-magnesium-iodide solution so prepared was syphoned over slowly into a flask containing 28.8 grams of levulinic ester and 25 cc. of absolute ether. After the mixture had stood for several hours, 10 cc. of absolute alcohol were added and then dry hydrobromic acid gas was passed in until saturated. The solution was allowed to stand over night and was then poured into ice water and extracted with ether. The extract was washed twice with water and dried over sodium sulfate. When the ether was distilled off, there remained 17 grams of a blackish colored residue.

0.3720 grams of this substance when decomposed with 10 cc. of ammonia, gave 0.1548 grams of silver bromide, or 49.6 per cent of the theory demanded by bromoisocaproic ester.

Dimethylcyanocarboxethylcyclopentanone.

For the preparation of this ketone from the isocaprolactone prepared from levulinic ester, the method was the same as has been previously described.

C. Condensation of Isobutylene Bromide with Cyanoacetic Ester.

Isobutylene Bromide.[1]

A mixture of five parts of isobutyl alcohol, five parts sulfuric acid, and one part of water was slowly dropped into a flask containing 96 cc. of isobutyl alcohol and 100 cc. of sulfuric acid maintained at a temperature of 160°-165°. In heating up the contents of the flask, it was found that at 110° it was necessary to remove the flame for a short time. At this temperature the reaction proceeds spontaneously for a while. The isobutylene so generated was passed thru an empty wash bottle, then thru dilute sodium hydroxide, and lastly into 40 cc. of bromine covered with a little water. After the decolorization of the bromine, it was transferred to a separatory funnel, washed with water and dilute sodium hydroxide, and dried over fused calcium chloride. The yield was 37.6 grams boiling at 64°-70° at 38-50 mm. pressure.

Dimethyldicyanoadipic Ester.

4.26 grams (two mols) of sodium were dissolved in 60 cc. of absolute alcohol and to the hot solution were added 21 grams (two mols) of cyanoacetic ester. 20 grams (one mol) of isobutylene bromide were added slowly thru the upright condenser. After boiling the solution until nearly neutral it was

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[1] Hell and Rothberg, Ber. d. chem. Ges. (1889) 22, 1738.

filtered hot, the precipitated sodium bromide being washed well with absolute alcohol. It was impossible to freeze out any crystalline substance from the alcoholic solution, so it was neutralized with hydrochloric acid and evaporated under diminished pressure. A variety of reagents were used in the attempt to crystallize this residue but in all cases only a gummy material could be obtained.

D. Zeissel[1] Determination of the Carboxethyl Group in Dimethylcyanocarboxethylcyclopentanone.

0.2572 grams of dimethylcyanocarboxethylcyclopentanone and 10 cc. of freshly prepared hydriodic acid* (sp. gr. 1.7) were heated to 100° in a 50 cc. distilling flask. The ethyl iodide generated was passed thru a condenser at a temperature of 80°C. and set at an angle of 30°. The vapor was then passed through Geissler bulbs containing red phosphorus and water, (the bulbs heated in a bath at 80°), and finally into an alcoholic silver nitrate solution. This solution was prepared by dissolving 2 grams of silver nitrate in 5 cc. of water, 45 cc. of absolute alcohol, and one drop of pure nitric acid. A steady stream of carbon dioxide was sent thru the apparatus.

The precipitate of silver iodide was decanted, washed three times with 30 cc. of water, then 20 cc. of dilute nitric

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[1] Meyer, Analyse und Konstitutionsermittelung organischer Verbindungen. Page 488.

*By titration with standard sodium thiosulfate it was found that a sample of Kahlbaum's hydriodic acid in several years had decomposed to the extent of 10.5 per cent.

acid were added, and the mixture was placed on the water bath for ten or fifteen minutes. In the meantime the decanted solution was diluted to 300 cc., three drops of nitric acid were added, and the solution was evaporated until the odor of alcohol had disappeared. The volume was brought back to 300 cc. by the addition of water, and the two quantities of silver iodide were filtered and weighed. 0.2523 grams of silver iodide were obtained which was equivalent to 87.4 per cent of the theory.

To the residue from the ketone was added some water and red phosphorus. After standing several hours it was extracted with ether but as the ether was discolored by iodine, it was treated with sodium thiosulfate solution. The ether was separated, dried, distilled, and there remained 0.073 grams of a yellowish substance. After washing it on a porous plate with alcohol and a little ether, a product was obtained which melted at 118°-152°. At 118° it suddenly turned brown and partially liquefied. There was not enough of this substance to purify further.

To the aqueous solution remaining from the extraction was added 25 cc.of a 30 per cent solution of sodium hydroxide. From this, 100 cc. were distilled over thru the Kjeldahl apparatus, and there was found 0.01287 grams of nitrogen or 74.58 per cent of the theory for the amount of the ketone used in the Zeissel determination.

E. 1,3,3-Trimethyl 2-cyan 2-carboxethylcyclopentanol-1.

Gordon's[1] method was used. 2.84 grams of methyl iodide in 50 cc. of absolute ether were slowly run into a flask containing 0.48 grams of magnesium ribbon covered with absolute ether. After all the magnesium had dissolved, the solution was slowly syphoned over into a flask containing 4.26 grams of dimethylcyancarboxethylcyclopentanone and 35 cc. of absolute ether. The syphon was washed out with 25 cc. more of absolute ether. The solution was acidified and the etherial solution separated and dried over anhydrous sodium sulfate. After distilling off the ether and crystallizing the residue from alcohol, there remained 1.46 grams of substance melting at 150°. This then was the unchanged ketone instead of the desired product which melts at 193.4°. The experiment was repeated with the same results.

In repeating the experiment the third time, using half quantities, 500 cc. of absolute ether were used in hopes of dissolving the ketone but the latter was nearly insoluble. Only the unchanged ketone was obtained after carrying out this experiment. Then a mixture of absolute ether and absolute benzene was tried but the results were the same. Finally absolute benzene alone was used to effect the solution of the ketone and a white crystalline compound was precipitated upon the addition of the etherial solution of magnesium-methyl-iodide. This was found to be the ketone.

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1. Gordon, Thesis University of Illinois (1911).

F. Dimethylcyanocarboxethylcyclopentane.

An attempt was made to effect the reduction of the ketone to the hydrocarbon by the method used so successfully by Clemmensen.[1] 5 grams of zinc were left for one hour in 10 cc. of a five per cent solution of mercuric chloride. After pouring off the liquid, 1.0095 grams of the ketone and 12 cc. of 1:3 hydrochloric acid were added. The solution was boiled for six hours, adding a little dilute hydrochloric acid from time to time, but there was no action apparent. Then enough alcohol was added to dissolve the ketone and also another lot of amalgamated zinc. After boiling nearly forty hours longer, only the unchanged ketone was obtained.

G. The Oxime of Dimethylcyanocarboxethylcyclopentanone.

1.0027 grams (one mol) of the ketone and 0.3332 grams (one and one-half mols) of hydroxylamine hydrochloride were dissolved in 30 cc. of warm absolute alcohol. Then 0.57 cc. (one and one-quarter mols) of sodium hydroxide solution (3 cc. equivalent to one gram NaOH) were added, and the mixture was boiled on the water bath for eight hours. A precipitate of sodium chloride was filtered hot and from the alcoholic solution was obtained 0.1 gram of ketone and a fairly good yield of the oxime. This was a white substance melting somewhat at 104° and mostly at 118°, being a mixture of isomers.

0.1056 grams of the oxime gave 12.05 cc. of nitrogen at 22.7° and 741.5 mm. pressure.

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[1] Orig. Com. 8th Int. Congr. App. Chem. (1912) 7, 68.

	Calculated for $C\ H\ O_3N_2$	Found
Nitrogen	12.52	12.65

0.305 grams (one mol) of the oxime and 1.48 cc. (3 mols) of a sodium hydroxide solution (1 cc. equivalent to 0.11 grams of NaOH) were put on the steam bath for eight hours. After acidifying the solution and evaporating off most of the water, a white crystalline compound (melting at 127°-129°) was deposited when cooled. It failed to give an odor of acetic acid when heated to decomposition.

This substnace was dissolved in ammonia, one mol of a calcium chloride solution was added, and the solution evaporated down to about five cc. The salt which separated was filtered off, dissolved in water, and reprecipitated by evaporating the solution. The salt dried at 140° for an hour gave 10 per cent of calcium when ignited and weighed as calcium oxide. Theory requires 15.8 per cent for the calcium salt of 3,3-dimethyl 2,2-dicarboxylic cyclopentanone oxime, while for calcium malonate there is required 36.3 per cent of calcium. It is thought that the low percentage of calcium found was due to an imperfect drying of the salt.

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